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(54) ACTIVE MATERIAL FOR LITHIUM BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide high energy density and a high voltage by providing an olivine structure and using a compound having a specified composition.

SOLUTION: This compound is represented by $\text{LiM}_{1-x}\text{M}_x\text{PO}_4$ (M: Co, Ni, Mn; Me: Mg, Fe, Ni, Co, Mn, Zn, Ge, Cu, Cr; $0 \leq x \leq 0.5$). Preferably, an olivine structure has an orthorhombic symmetry having an orthorhombic symmetry space group Pmnb. Also, when the values (a), (b) and (c) of the unit grating parameter of an orthorhombic phase are LiMnPO_4 , LiNiPO_4 , and LiCoPO_4 , these are preferably values within specified different ranges. Preferably, the compound having the olivine structure is included in an electrode as a positive electrode active material for a lithium battery, and preferably a negative electrode active material selected from this, electrolytic liquid, Li, and Li alloy, Li_xSnO_2 and a carbon material is provided in the battery.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[The technical field to which invention belongs] this invention relates to improvement of a lithium cell.

[Description of the Prior Art] With rapid progress and a rapid miniaturization of electronics, it is reliable, and it is lightweight and the cell which has high-energy density is needed. A lithium cell is promising about this point. The lithium cell has high voltage and a high energy density, and is because the life is long. However, development of the lithium cell which can be charged because of the problem of chemical reactivity with almost all the nonaqueous electrolyte that a metal Li anode presents, and the safety relevant to Metal Li has been barred for several years. Recently, it has a new interest in the secondary lithium cell. This relates to producing a "lithium ion" cell by using Li insertion compound as an anode instead of Metal Li. However, it is necessary to pay attention to selection of a cathode host and an anode host by this system. Stratified $\text{LiMO}_2(\text{M:Co, nickel})$ [Mat. Res. Bull. 15 (1980) 783 and J. Appl. Phys. As for the 19 (1980) 305] and three-dimensions spinel type oxide LiMn_2O_4 [Mat. Res. Bull. 18 (1983) 461 and Mat. Res. Bull. 19 (1984) 179], electric discharge middle voltage should receive a lithium. It is in the position of about 4 V, and has become an attractive cathode for lithium ion batteries. Furthermore, research of whether the cathode material of other molds can use it by the lithium ion system was recently made. These compounds consist of Nasicon related 3D frames, such as $\text{LiXM}_2(\text{PO}_4)_3 (\text{M:Ti, V, Fe})$ and $\text{M}_2(\text{SO}_4)_3(\text{M:Ti, Fe})$ [Solid State Ionic 92 (1996) 1].

[Problem(s) to be Solved by the Invention] The technical problem of this invention is offering the active material for lithium cells which can obtain the high voltage by the high-energy density which was not attained in the conventional positive active material.

[Means for Solving the Problem] The summary of this invention is a formula usable as a positive active material for lithium secondary batteries. $(0 (\text{Me:Mg, Fe, nickel, Co, Mn, Zn, germanium, Cu, Cr}) \leq x \leq 0.5)$ It is expressed with $\text{LiM}_1\text{-XMeXPO}_4$ (M:Co, nickel, Mn), and these are characterized by presenting the olivine structure of having prismatic-crystal type symmetric property and a space group Pmn_b .

[Embodiments of the Invention]

[Example] Next, although an example explains this invention with reference to an attached drawing with reference to the experiment which this invention person conducted, it is not limited to this.

[example 1] Li_2 -- LiMnPO_4 of this invention was prepared by CO_3 , MnCO_3 , and (NH_4) the one-step reaction using the mixture of the stoichiometry which consists of 2HPO_4 . This mixture was first mashed with the agate mortar, it pressurized by 400 kgf/cm^2 and was made the pellet, and next, in 450 degrees C, in air, it calcined for 4 hours and heated in 800 degrees C after that for 24 hours.

[example 2] Li_2 -- as CO_3 , MnCO_3 , $2(\text{NH}_4) \text{HPO}_4$, and any 1 of next, i.e., an iron source of supply $\text{LiMn}_1\text{-XMeXPO}_4$ (Me:Mg, nickel, Co, Fe) of this invention was prepared by the one-step reaction using the mixture of the stoichiometry which consists of NiO as Co_3O_4 or a nickel source of supply as MgO and a cobalt source of supply as FeC_2O_4 , $2\text{H}_2\text{O}$, and a magnesium source of supply. This mixture was first mashed with the agate mortar, it pressurized by 400 kgf/cm^2 and was made the pellet, and next, in 450 degrees C, in air, it calcined for 4 hours and heated in 800 degrees C after that for 24 hours. When doping iron, calcining was performed under the nitrogen flow.

[example 3] Li_2 -- LiNiPO_4 of this invention was prepared by the one-step reaction using the mixture of the stoichiometry which consists of CO_3 , NiO , and $(\text{NH}_4) 2\text{HPO}_4$. This mixture was first mashed with the agate mortar, it pressurized by 400 kgf/cm^2 and was made the pellet, and next, by 350-degree-C smell, under the nitrogen flow, it calcined for 8 hours and heated in 750 degrees C after that for 15 hours.

[example 4] Li_2 -- as CO_3 , MnCO_3 , $2(\text{NH}_4) \text{HPO}_4$, and any 1 of next, i.e., an iron source of supply $\text{LiNi}_1\text{-XMeXPO}_4$ $(0 \leq x \leq 0.5)$ (Me:Mg, Mn, Co, Fe) of this invention was prepared by the one-step reaction using the mixture of the stoichiometry which consists of MnCO_3 as Co_3O_4 or a manganese source of supply as MgO and a cobalt source of supply as FeC_2O_4 , $2\text{H}_2\text{O}$, and a magnesium source of supply. This mixture was first mashed with the agate mortar, it pressurized by 400 kgf/cm^2 and was made the pellet, and next, in 350 degrees C, in air, it calcined for 8 hours and heated in 750 degrees C after that for 24 hours. When doping iron, calcining was performed under the nitrogen flow.

LiCoPO_4 of this invention was prepared by [example 5] Li_2CO_3 , Co_3O_4 , and (NH_4) the two-step reaction using the mixture of the stoichiometry which consists of 2HPO_4 . This mixture was first mashed with the agate mortar, and it pressurized by 400 kgf/cm^2 , was made the pellet, and, next, calcined in air by 350-degree-C smell for 9 hours. This matter was cooled and mashed, and it pressurized by 400 kgf/cm^2 again, was made the pellet, and heated in 750 degrees C after that for 30 hours.

As [example 6] Li_2CO_3 , Co_3O_4 , $2(\text{NH}_4) \text{HPO}_4$, and any 1 of next, i.e., an iron source of supply. $\text{LiCo}_1\text{-XMeXPO}_4$

$0 \leq x \leq 0.5$) (Me: Mg, Mn, nickel, Fe) of this invention was prepared by the one-step reaction using the mixture of the stoichiometry which consists of MnCO_3 as NiO or a manganese source of supply as MgO and a nickel source of supply as $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and a magnesium source of supply. This mixture was first mashed with the agate mortar, it pressurized by 400 kgf/cm^2 and was made the pellet, and next, in 350 degrees C, in air, it calcined for 8 hours and heated in 750 degrees C after that for 24 hours. When doping iron, calcining was performed under the nitrogen flow. Drawing 1 A, and 1B and 1C express the pure X diffraction pattern of LiMnPO_4 , LiNiPO_4 , and LiCoPO_4 obtained according to this invention, respectively. Each of three X diffraction patterns can belong to prismatic-crystal type symmetric property and a space group Pmnb. The unit-lattice parameter of LiMnPO_4 drawn after attribution of the X diffraction pattern of LiMnPO_4 , Unit-lattice parameters [as opposed to $a = 5.86 \times 0.5 \text{ \AA}$, $b = 10.07 \times 0.2 \text{ \AA}$, and $c = 4.68 \times 0.5 \text{ \AA}$; LiCoPO_4 in $a = 6.11 \times 0.5 \text{ \AA}$, $b = 10.46 \times 0.5 \text{ \AA}$, and the unit-lattice parameter to $c = 4.73 \times 0.5 \text{ \AA}$; LiNiPO_4] are $a = 5.92 \times 0.5 \text{ \AA}$, $b = 10.21 \times 0.5 \text{ \AA}$, and $c = 4.70 \times 0.5 \text{ \AA}$. Drawing 2 expresses an example of the cyclic voltammetry of LiCoPO_4 . This matter presents one oxidization peak to the position of 5.1V, and presents one reduction peak to the position of 4.7V. Furthermore, although another strong reduction peak was observed by the 0.7V neighborhood, the corresponding oxidization peak was not observed. In this case, LiPF_6 dissolved in the sulfolane by which bearing to 6V is known was used as the electrolytic solution. Drawing 3 expresses the charge and discharge of the first cycle of the matter LiCoPO_4 of this invention. The examination was carried out in the current density of 0.1 mA/cm^2 in the battery case made from Teflon which used the LiPF_6 + sulfolane as the electrolytic solution. This cell is equipped with the negative electrode (the active material of 87% of this invention, 5% of carbon black, composition of 8% of PVDF), the lithium counter electrode, and the lithium reference electrode. First, this cell is charged, and a lithium is extracted from the matter of this invention, next it discharges, and a lithium ion is inserted and returned. This cell presents a flat part to the position of 4.7V during electric discharge, and capacity is 80 mAh/g . However, charge capacity is slightly high and is about 105 mAh/g . Although this value is still lower than geometric capacity 167 mAh/g in the case of carrying out extraction insertion of the one lithium, it is shown that it can improve by optimizing manufacture conditions. Drawing 4 expresses the charge and discharge of the first cycle eye of the matter LiCoPO_4 of this invention. An examination is in the Teflon battery case of the type which used the LiPF_6 + sulfolane as the electrolytic solution. It carried out in the current density of 0.1 mA/cm^2 . The potential range of the charge and discharge of this cell was $1 \leq V \leq 5.3$. During electric discharge, the flat part was observed by the position of 4.7V, and also another flat part was observed by the 1V neighborhood. The capacity as the whole is very high and is about 350 mAh/g .

[Effect of the Invention] Formula which has the olivine type structure of this invention The active material expressed with $\text{LiM}_1\text{-XMeXPO}_4$ (M: Co, nickel, Mn, Me: Mg, Fe, nickel, Co, Mn, Zn, germanium, Cu, Cr) ($0 \leq x \leq 0.5$) is as a positive active material at a lithium ion fuel cell subsystem. It is usable, capacity is as large as 170 mAh/g , and, moreover, potential has the outstanding effect of being high, with 5V.

[Translation done.]